

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Appln. No: 10/527,633
Applicants: Martyn Vincent Twigg et al.
Filed: October 7, 2005
Title: PROCESS FOR TREATING COMPRESSION IGNITION ENGINE EXHAUST GAS
T.C./A.U.: 1793
Examiner: Timothy C. Vanoy
Confirmation No.: 2150
Docket No.: JMYT-348US

DECLARATION UNDER 37 C.F.R. §1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Raj Rao Rajaram, hereby declare that:

1. I received a Bachelor of Science degree in Industrial Chemistry from Brunel University, London, United Kingdom in 1980 and a Doctor of Philosophy, also from Brunel University in 1983. I have over twenty years of work experience in the area of developing catalysts for treating exhaust gas emissions from spark-ignition and compression ignition engines, specifically gasoline and diesel engines. I am currently employed by Johnson Matthey PLC as Scientific Consultant.

2. I conducted or oversaw the majority of the experiments provided as Examples in the Applicants' patent specification. I have also reviewed the claims and the specification of the present application. Based on this review, I believe that I have an understanding of the invention recited in the claims of the present application.

3. It is my understanding that the present application, as recited for example in claim 9, involves an apparatus comprising a diesel engine, a means for controlling an operating mode of the engine and an engine exhaust system. I understand that the engine exhaust system includes a catalyst including palladium (Pd) supported on a support material and at

least one base metal promoter associated with the palladium, wherein the at least one base metal promoter comprises at least one reducible oxide. The operating mode is defined wherein substantially all fuel for combustion in the engine is injected into a combustion chamber of the engine prior to the start of combustion during at least a portion of an engine cycle.

4. I have also reviewed the Office Action, dated December 20, 2007, in which the Office, at page 4, has rejected (among other rejections) claims 9, 11-18, 22-24, 28, 33-35, 40, 44 and 47-52 as unpatentable over EP 0 341 832 ("Cooper") in view of Applicants' alleged admission set forth on pgs. 1 and 2 in their specification.

5. I understand that the Office asserts, at page 5, that "[t]he Cooper et al. reference describes an apparatus, diesel engine and method for removing contaminants (i.e. NO_x, etc.) out of the exhaust gas emitted from a diesel engine by passing the exhaust gas through a filter that may support both 'a catalyst to catalytically generate oxidant NO₂ in situ . . . as well as base metal catalysts . . . (please see pg. 2 in 54 to pg. 3 in 2).'" (emphasis in original).

6. I am familiar with diesel engine exhaust gas treatment technology, and in particular diesel engine exhaust gas filter systems such as the one described in Cooper, and the catalysts used in such filter systems.

7. I am also familiar with the enclosed documents:

- (1) U.S. Patent No. 5,157,007 ("Domesle");
- (2) Wyatt, M. et al., THE DESIGN OF FLOW-THROUGH DIESEL OXIDATION CATALYSTS, presented at the Society of Automotive Engineers (SAE), International Congress in Detroit, Michigan, USA on 1-5 March 1993, pp. 57-69 (1993) ("Wyatt");
- (3) Boreskov, G.K., "Catalytic Activation of Dioxygen", Chapter 2 in CATALYSIS, Science and Technology, edited by Anderson, John R. et al., Vol. 3, pp. 50-55, 129 (1982) ("Boreskov"); and
- (4) Jelles, S.J. et al., MOLten SALts AS PROMISING CATALYSTS FOR OXIDATION OF DIESEL SOOT: IMPORTANCE OF EXPERIMENTAL CONDITIONS IN TESTING PROCEDURES, Applied Catalysis B: Environmental 21, pp. 35-49 (1999) ("Jelles").

8. As I understand from page 5 of the Office Action, the Office considers the base metal catalysts disclosed in Cooper, which are "typically a catalyst comprising lanthanum, cesium and vanadium pentoside ($\text{La/Cs/V}_2\text{O}_5$) or the like" (Cooper, at page 3, lines 1-4) or vanadium oxide *per se* (Cooper, at page 3, line 36), to be analogous to the "at least one base metal promoter" recited in the pending claims.

9. The Domesle reference is directed to "[a]n open-cell, monolith catalyst for the purification of diesel-engine exhaust gas with a coating of finely divided inorganic oxides containing vanadium and platinum group metal as active components." (See Abstract). Referring to Tables 1 and 2 of Domesle, and in particular Examples 10, 11, 12 and 20, Domesle reports the light-off temperature at which 50% of CO is converted (T_{50}) for Pd-containing catalysts. As set forth in Table 1, Examples 10, 11 include Pt:Pd = 2:1, Pt:Pd = 1:3, respectively, and Examples 12 and 20 include Pd only, each for 1.5 g/dm³ noble metal loadings. For each of these Examples, V_2O_5 is also included at a loading of 5 g/dm³, and the carrier material is 140 g/dm³ Al_2O_3 , except for Example 20, which includes 60 g/dm³ Al_2O_3 and 80 g/dm³ SiO_2 . Example 3 (ref.), used as a reference example in Domesle, does not include any V_2O_5 . As shown in Table 2 of Domesle, Example 3 (ref.) has a T_{50} of 235°C, a SO_2 conversion at 350°C of 55% and a SO_2 conversion at 450°C of 63%. In comparison, Examples 10, 11, 12 and 20 have T_{50} for CO conversion of 238°C, 242°C, 260°C and 255°C, respectively, SO_2 conversion at 350°C of 15%, 16%, 8% and 7%, respectively, and SO_2 conversion at 450°C of 28%, 24%, 17% and 19%, respectively. Moreover, conversion of CO at 350°C for Example 3 (ref.) is reported at 89%, compared to 90%, 88%, 85%, and 85%, for Examples 10, 11, 12 and 20, respectively. Also of note in Domesle are the reported conversions, in Table 3, of some of the catalysts listed in Tables 1 and 2 after 100 hours of engine endurance testing at 550°C exhaust gas temperature. As listed in Table 3, Example 3 (ref.) has a T_{50} for CO conversion of 245°C, SO_2 conversion at 350°C of 32% and SO_2 conversion at 450°C of 60%. In comparison, Examples 10, 11 and 12 have T_{50} CO conversions of 240°C, 275°C and 280°C, respectively, SO_2 conversions at 350°C of 0%, 3% and 7%, respectively, and SO_2 conversions at 450°C of 11%, 17% and 20%, respectively. As is apparent from the data presented in Tables 1, 2 and 3 of Domesle, the inclusion of V_2O_5 in Pt:Pd or Pd-only catalysts has no promotion effect for T_{50} CO conversion, but a significant impact on inhibiting SO_2 conversion as compared to similar catalysts without V_2O_5 . While there is no Pd-only reference in Domesle, I would expect that the

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lack of promotion (and evidence of poisoning effect shown in the Wyatt reference discussed below) for vanadium would be repeated for a Pd/alumina catalyst in which palladium is the only platinum group metal.

10. Similar to the Domesle reference, the Wyatt reference is directed to the development of a catalyst that can provide good particulate control and is capable of oxidizing HC, CO and soluble hydrocarbon fraction (SOF) with minimal oxidation of SO₂ for diesel engines. Of particular significance is that Wyatt discusses the effect of addition of base metal modifiers by searching for a selective poison for Pt/alumina that would reduce the activity of Pt for SO₂ oxidation while maintaining the good activity of Pt for HC and CO oxidation. As shown in Table 3, the T₅₀ for CO oxidation with no base metal promoter is 125°C, but increases to 146°C with the addition of vanadium (V), i.e. the presence of vanadium actually suppresses the CO oxidation activity of the Pt/alumina. In comparison, the CO T₅₀ remained unchanged at 125°C with the addition of Mn, i.e. no promotion effect was observed. As shown in Table 4, addition of V is effective in reducing the SO₂ conversion to SO₃ to 27% at 450°C, with a T₅₀ of 493°C, as compared to 97% conversion with no base metal added, with a T₅₀ of 275°C, and 85% with addition of Mn, with a T₅₀ of 296°C. As can be seen from Wyatt, for Pt/alumina catalysts the addition of the base metal V was effective in reducing SO₂ conversion. However, as noted in Wyatt, "no additive in this set significantly promotes the activity for Pt for either HC or CO." (Wyatt, at page 62). Rather, "as noted earlier, the CO and propene conversions are relatively unaffected by the addition of V" (Wyatt, at page 62). Wyatt observes that "a relatively small suppression of propene and CO performance is observed together with dramatic suppression of SO₂ oxidation activity. These results are consistent with the ongoing interest in the use of vanadium and metal vanadates in the formulation of catalysts for diesel particulate traps (18-21) and for flow-through oxidation systems 22,23)." (Wyatt, at page 63). I believe that an explanation for why there is no CO oxidation promotion for vanadium seen in the Domesle reference, but that a suppression of CO oxidation for vanadium is reported in the Wyatt reference, is that Wyatt used more vanadium (5wt% by my calculation) than Domesle (3wt% vanadium). As mentioned below in connection with the Jelles reference, vanadium oxides are molten at relatively low temperatures, so the suppression of CO oxidation observed by Wyatt may be due to blocking of active sites. Additionally, although Wyatt found no promotion effect when Mn was added to Pt/alumina, we actually found that MnO₂ promotes oxidation of CO by palladium (see Example 6 in the present application).

11. Basis for why I would not expect vanadium oxide to promote palladium in the apparatus according to the invention is in the Boreskov reference. Here, as shown on page 53, Figure 10, the oxygen binding energy for V_2O_5 , according to references 31-33 cited in Boreskov, is illustrated to be approximately 180 kJ mol^{-1} . In comparison, the oxygen binding energies for MnO_2 , Fe_2O_3 , Co_3O_4 and CuO are approximately 85 kJ mol^{-1} , 140 kJ mol^{-1} , 60 kJ mol^{-1} and 65 kJ mol^{-1} , respectively. In other words, the graph depicts the relative amount of energy required to desorb oxygen from the respective oxides. As shown, V_2O_5 requires an amount of energy significantly higher than MnO_2 , Fe_2O_3 , Co_3O_4 and CuO for oxygen desorption. What this means in practice is that V_2O_5 would desorb oxygen at a higher temperature than the other reducible oxides. Where a preferred reducible oxide is combined with palladium, oxygen desorbed from the reducible oxide is made available to the palladium (so-called "spillover") for oxidizing CO to CO_2 . In the present invention, the promotion effect of the reducible oxides is relevant at lower temperatures. In Example 1 of the present application, it is shown that the T_{80} for CO oxidation for an unpromoted palladium catalyst (Catalyst B - 2wt% Pd-alumina-based catalyst) is higher than the $CO T_{80}$ for the equivalent promoted palladium catalyst (Catalyst C - 2wt% Pd-ceria-containing catalyst), e.g. for Gas Mixture 2, Catalyst B has a $CO T_{80}$ of 247°C , whereas Catalyst C has a $CO T_{80}$ of 170°C . This example shows that palladium will oxidize CO in the absence of a promoter at 247°C , so if the palladium is combined with a reducible oxide that does not desorb oxygen below 247°C , the reducible oxide cannot promote the CO oxidation reaction of palladium, i.e. the reducible oxide would be merely a "spectator". For this reason, I believe that no promotion effect for vanadium is seen in the examples of the Domesle reference. By contrast, it can be seen that in Example 1 of Applicants' patent specification, Catalyst C reduces the $CO T_{80}$ relative to Catalyst B from 247°C to 170°C , which is evidence for a promotion effect that I consider to be based on the relatively low oxygen binding energy of CeO_2 .

12. The Cooper reference states that a base metal catalyst coating on the filter, e.g. vanadium oxide or preferably $La/Cs/V_2O_5$ "facilitates higher temperature combustion [of particulates]" (Cooper at page 3, lines 34-37). It is my understanding that the mechanism for combusting particulates on a filter using V_2O_5 or $La/Cs/V_2O_5$ is different from that of promoting palladium CO oxidation using oxygen "spillover", because the particulate combustion mechanism requires direct contact between the molten catalyst and the particulate. This difference is illustrated by the Jelles reference. In the Jelles reference, three eutectic mixtures

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studied were $\text{Cs}_2\text{MoO}_4\text{-V}_2\text{O}_5$, $\text{CsVO}_3\text{-MoO}_3$ and $\text{Cs}_2\text{SO}_4\text{-V}_2\text{O}_5$ to demonstrate their potential as soot oxidation catalysts and the activity of these catalysts is compared with, among others, V_2O_5 *per se* (compare Figures 3 and 4 in Jelles on page 40). As mentioned in the abstract, the catalysts were characterized as having a high activity above their melting point of about 625 K, explained by better contact between the soot and the catalyst most likely achieved by wetting of the soot by the liquid catalyst. As described at Section 4.2, page 46 of Jelles, "[f]rom the catalyst stability experiments, it is clear that the contact between the soot and the catalyst is not the result of catalyst vapour, and therefore, it is concluded that the mobility is a result of the liquid phase, in other words of catalyst surface migration." According to Jelles, droplet formation, as shown in Figures 13-15, confirms this conclusion. (Jelles, at page 46). As evidenced by Jelles, cesium-vanadium catalysts, or V_2O_5 catalysts, are low melting point molten base metal combustion catalysts that interact with soot in a liquid-phase interaction. Furthermore, Jelles explains that "[t]he exact mechanism of oxidation is yet unclear, but a Mars and van Krevelen route could be very well part of it. Rapid transport of electrons and ions through the ionic liquid could be an important parameter." (Jelles, at page 47)

13. Based on the above information, it is my opinion that one of ordinary skill in the art would not have expected the base metal catalysts of Cooper, namely, a catalyst comprising lanthanum, cesium and vanadium pentoxide or vanadium pentoxide *per se*, as suggested by the Office, to function as a base metal promoter in the claimed invention.

14. As evidenced by the Domesle reference, the V_2O_5 base metal would have been expected to have little or no effect on the oxidation activity of the palladium in the claimed catalyst. The inclusion of V_2O_5 in Pt:Pd or Pd-only catalysts has no impact on CO conversion, but significantly suppresses SO_2 conversion. Thus, V_2O_5 does not function as a catalyst promoter, especially for CO oxidation.

15. As shown by Wyatt, for Pt/alumina catalysts the addition of increased quantities of vanadium is effective in reducing SO_2 conversion, but also actually suppresses CO oxidation of the Pt/alumina catalyst. Although Wyatt's results, as reported in Tables 3 and 4, are for Pt/alumina catalysts, it is my opinion that a person of ordinary skill in the art would have expected to see a similar suppression of CO oxidation when vanadium is added to a Pd/alumina catalyst. In addition, Wyatt supports this position based on Figures 3 and 4. Figure 3

illustrates a laboratory reactor oxidation activity of Pt/alumina and Figure 4 depicts a laboratory reactor oxidation activity of Pd/alumina. Thus, although not identical in CO conversion (%) or the temperatures at which the CO conversions occur, the depicted CO conversions for Pt/alumina and Pd/alumina follow a similar trend. It is my opinion, therefore, that Wyatt also supports the conclusion that V_2O_5 is not a catalyst promoter. Moreover, if Wyatt supports any effect of V_2O_5 on oxidation, that effect would be the suppression, not promotion, of oxidation.

16. Further, as described in Boreskov, the oxygen binding energy of V_2O_5 requires an amount of energy significantly higher than MnO_2 , Fe_2O_3 , Co_3O_4 and CuO for oxygen desorption. Thus, V_2O_5 is less likely to be effective as a promoter than MnO_2 , Fe_2O_3 , Co_3O_4 and CuO , which are among those, or similar to those, described and/or claimed by Applicants. It is my opinion based on the binding energies presented for V_2O_5 and the Examples provided in the present application that Boreskov supports the position that one of ordinary skill in the art would not have chosen V_2O_5 as a base metal promoter for a diesel oxidation catalyst.

17. By my signature below, I hereby declare that all statements made in this document of my own knowledge are true, and that all statements made on information and belief are believed to be true. Further, I hereby declare that these statements are made with the knowledge that willful false statements, and the like so made, are punishable by fine or imprisonment, or both, under Section 1001, Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing on the application.

Respectfully submitted,



Raj Rao Rajaram

Dated: 20/06/08.